

# The Effect of Pressure on the Pyrolysis of Newsprint

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## Introduction

There is national concern over the disposal of solid municipal waste. Several pyrolysis plants designed to convert such waste into useful products have proven uneconomical. To help provide a stronger data base for improved pyrolysis processes, we have been studying the thermal chemistry of newsprint, the principle cellulosic material in urban waste. Previously, we have reported on the rate of degradation at low pressure, where secondary reactions of pyrolysis products are negligible (1). This paper discusses the influence of ambient pressure on newsprint pyrolysed at 340°C.

Since a dilute acid wash pre-treatment has been shown to significantly alter product yields from newsprint pyrolysis (2), we have examined both untreated and 1% HCl washed newsprint.

Pyrolysis of any lignocellulosic material gives a host of different products which are usually classified as either chars, tars, or gases depending upon their volatility. Chars are carbonaceous products, such as charcoal, that are not volatile. Tars are relatively high molecular weight compounds that are volatile only at pyrolysis temperatures; and gases are those products having readily measureable vapor pressures at room temperature.

Several investigators have shown, using a variety of cellulosic materials, ranging from cotton cellulose to wood, that pyrolysis in nitrogen at atmospheric pressure results in lower tar yields and greater gas and char formation than pyrolysis in a strong vacuum (3, 4). This difference in yields has been interpreted as due to secondary decomposition of tar molecules whose ability to escape from the reacting substrate is reduced at higher pressures. While the effect of ambient pressure on pyrolysis yields is qualitatively understood, there exists little quantitative information that allows mathematical modeling of this phenomena and, thereby, a clear link between low pressure pyrolysis experiments, used to study fundamental reaction kinetics, and industrial pyrolysis processes carried out at atmospheric pressure.

## Experimental Procedures

A sketch of our experimental apparatus is shown in Figure 1. Since a detailed account of our procedures is provided in reference (1), only a brief outline will be given here.

100 mg samples of dry, shredded newsprint are weighed into a small aluminum foil boat. The boat is sealed into a cool end of the reactor and a vacuum is drawn on the system. If we are examining the effects of ambient pressure, nitrogen is bled slowly into the system. Then the pyrolysis chamber is brought to a temperature slightly above that of pyrolysis. Next, power is reduced to that necessary for maintaining pyrolysis temperature and the sample boat is quickly brought to the center of the pyrolysis zone by means of a hand held magnet. Sample temperature is continuously monitored by a thermocouple embedded in the newsprint.

After a set time period, the boat is quickly withdrawn from the pyrolysis chamber, the cold traps are sealed off, and the reactor is allowed to cool.

The weight of residue in the sample boat is measured, and the tar products are rinsed off the cool glass walls of the reactor's side arms into tared vials. In this manner we can measure the weights of residue and tar as a function of pyrolysis time and pressure.

#### Theory

Our basic assumptions are that secondary decomposition of tar molecules is negligible in pyrolysis experiments below one torr, and that,  $\Delta W_t$ , the difference between  $W_t$ , the weight of tar obtained below one torr, and  $W_t'$ , the weight of tar formed at higher pressure, is a direct measure of the amount of secondary reaction.

A tar molecule may undergo two types of secondary reactions, decomposition to char and gases and repolymerization with the substrate. If each type of reaction is homogeneous and first order in tar, the rate of secondary reaction is

$$\frac{d\Delta W_t}{dt} = (k_d + k_r) W_t'' \quad (1)$$

where  $k_d$  and  $k_r$  are the rate constants for decomposition and repolymerization, respectively, and  $W_t''$  is the weight of tar molecules within the heated newsprint.

Diffusion coefficients in low pressure gases are inversely proportional to pressure. Therefore, if the tars rate of escape from the newsprint is taken as proportional to the amount of tar in the newsprint and inversely proportional to pressure, then

$$\frac{dW_t'}{dt} = \frac{\kappa}{P} W_t'' \quad (2)$$

where  $\kappa$  is the escape rate per unit weight per unit pressure.

If  $k_d$ ,  $k_r$  and  $\kappa$  are independent of time, then the ratio of equations 1 and 2 implies that for any time interval during which the amount of repolymerized tar is unimportant relative to the amount of unreacted newsprint

$$\frac{\Delta W_t}{W_t'} = \frac{(k_d + k_r)}{\kappa} P \quad (3)$$

Similarly, when reaction of repolymerized tar is unimportant, the fractional conversion to char via secondary decomposition may be expressed

$$\frac{\Delta R}{\Delta W_t} = \frac{f_d k_d + k_r}{k_d + k_r} \quad (4)$$

For longer pyrolysis times, when the fate of repolymerized tar molecules must be considered

$$\frac{\Delta R}{\Delta W_t} = \frac{f_d k_d + f_r k_r}{k_d + k_r} \quad (5)$$

where  $\Delta R$  is the difference in the weight of residue (char) between higher and very low pressure pyrolyses,  $f_d$  is the weight fraction of any tar molecule undergoing secondary decomposition that becomes char, and  $f_r$  is the average weight of char resulting from repolymerization of one tar molecule. If the repolymerization reaction disrupts the tar molecule's ring structure, the repolymerized compound may be predisposed to form char and gases.

An interesting parameter to consider is the ratio of the amount of tar escaping from the substrate during any given time interval at higher pressure to the amount of tar formed in the same time interval at very low pressure. If all repolymerized material eventually decomposes to char and gases, then this ratio is

$$\frac{W_t'}{W_t} = \frac{N/P}{(N/P) + k_d + k_r} \quad (6)$$

If a repolymerized tar molecule can be regenerated, then this ratio will be larger than the value predicted by equation 6. However, should the breakdown to char of the repolymerized material induce or catalyze substrate conversion to char, then the  $W_t'/W_t$  ratio will be less than predicted by equation 6.

## Results

The influence of ambient pressure on pyrolysis yields is illustrated in Figure 2. The weight of tar products and the weight of sample residue is plotted versus time, comparing 700 torr and below one torr pyrolyses of 100 mg of acid washed newsprint at 340°C. The ultimate tar yield at 700 torr is 34 % less than at very low pressure, while the final weight of residue (char) is 32 % greater at 700 torr. Notice that at both pressures there is an initial rapid generation of tar.

In our previous paper we noted that the thermal degradation of newsprint occurs in two stages: a fast initial degradation, that can be modeled as a zeroth order reaction; and a subsequent, slower degradation that is first order in remaining newsprint. At 340°C, the rapid, early degradation is over within three minutes of the sample's entry into the pyrolysis zone. This initial reaction accounts for 68 % of the ultimate tar production. As seen in Figure 2, the remaining 32 % of the tar is produced largely during the next sixty minutes of pyrolysis, while the degradation reaction follows a first order rate law.

Table 2 gives data describing the secondary decomposition during the first three minutes of pyrolysis. The fractional extent of secondary tar decomposition and  $\Delta R/\Delta W_t$  are listed for both acid washed and untreated newsprint. For each substrate, the extent of secondary decomposition increases uniformly with ambient pressure. The change in the sample residue is nearly a constant fraction of the change in weight of recovered tar.  $\Delta R/\Delta W_t$  is not a function of ambient pressure.

The ratio of the amount of secondary reaction to the amount of recovered tar is plotted versus pressure in Figure 3, for the initial degradation of both acid washed and untreated newsprint. As predicted by equation 3, the data are well fit by a straight line passing through the origin. Linear least square fits to the data that are constrained to pass through the origin are included in Figure 3. The slopes of these lines are reported in Table 1 along with their 95% confidence limits. From equation (3), these slopes represent the ratio of the rate of secondary tar reaction to the rate of tar escape per unit pressure. The larger value obtained for the acid washed newsprint suggests that the tars produced from acid washed newsprint are more reactive than the tars arising from untreated newsprint.

As seen from equation 4, the magnitude of the  $\Delta R/\Delta W_t$  ratio depends on two factors,  $f_d$ , the fractional char yield during secondary decomposition, and  $k_d/k_r$ , the ratio of the rate of decomposition to the rate of repolymerization.

If we arbitrarily adopt a value for  $f_d$  of 0.2, the ultimate char yield in low pressure pyrolyses, then the  $k_d/k_p$  ratios implied by the  $R/W_t$  results are 7.0 and 0.6 for the acid washed and untreated newsprint, respectively. The point is that, irrespective of the  $f_d$  value, the repolymerization reactions are relatively more important in the untreated than in the acid washed newsprint.

Insight into the types of secondary reactions that occur at longer pyrolysis times can be gathered from the data in Table 2. At longer times the amount of repolymerized material will no longer be small in regard to the amount of remaining substrate. The ultimate  $R/AW_t$  ratios are given in Table 2 for both acid washed and untreated substrates. These ratios show no pressure dependence, but they are slightly higher than the corresponding ratios at the end of only three minutes pyrolysis time. This suggests that char forming reactions are more prevalent at longer pyrolysis times.

Table 2 also lists the ratio of the amount of tar recovered in higher pressure experiments to the amount of tar formed in low pressure pyrolyses for pyrolysis times greater than three minutes. Also included in Table 2 is the value predicted for this ratio by equation 6, based on the assumption that all repolymerized material eventually forms either char or gases. Agreement between the experimental and predicted quantities is poor only for the lowest pressures, where the measured values fall below those given by equation 6. This implies some ability of the repolymerized material to catalyze char formation in the substrate, although the effect is subtle and readily masked at higher loadings of repolymerized tar.

#### Summary

We have developed a simple model, based upon homogeneous first order reactions, for describing the influence of ambient pressure on newsprint pyrolysis. Values for the relative rates of secondary tar reaction to tar escape per unit pressure have been obtained for acid washed and untreated newsprint. Tars from the acid washed material are more apt to decompose while tars from untreated newsprint have a greater likelihood of repolymerizing and then catalyzing char formation.

#### References

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Table 1 - Early Secondary Decomposition Reactions

Pressure (torr)	Acid Washed Newsprint		Untreated Newsprint	
	$\frac{\Delta W_t}{W_t} 3 \text{ min}$	$\frac{\Delta R}{\Delta W_t} 3 \text{ min}$	$\frac{\Delta W_t}{W_t} 3 \text{ min}$	$\frac{\Delta R}{\Delta W_t} 3 \text{ min}$
100	.072	.33	.026	.80
175	.13	.30	.036	.64
400	.27	.28	.11	.73
700	.35	.29	.18	.73

$$\frac{k_d + k_r}{\chi} (\text{torr}^{-1}) \quad 8.15 \pm .33 \times 10^{-4} \quad 3.07 \pm .07 \times 10^{-4}$$

Table 2 - Longer Time Secondary Reaction Data

Pressure (torr)	$\frac{\Delta R}{\Delta W_t} \infty$	$\frac{W_{t\infty} - W_{t3}}{W_{t\infty} - W_{t3}}$	$\frac{\chi/P}{\chi/P + k_d + k_r}$	
100	.37	.75	.93	Acid Washed Newsprint
400	.36	.77	.75	
700	.40	.69	.64	
175	.76	.90	.95	Untreated Newsprint
400	.81	.88	.89	
700	.84	.82	.82	

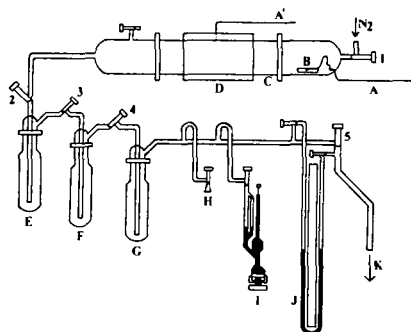


Fig. 1. Experimental apparatus: (A,A') thermocouple wires; (B) sample boat; (C) Pyrex cylinder; (D) insulated, quartz pyrolysis zone; (E, F, G) cold traps; (H) sample port; (I) McLeod gauge; (J) manometer; (K) connection to vacuum pump; (1-5) PTFE valves.

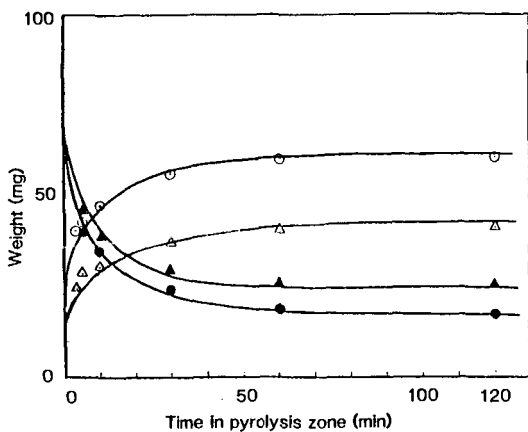


Fig 2. Influence of ambient pressure on pyrolysis yields at 340 C. Open figures represent tars and solids represent residue. Pressures are 1 torr (○) and 700 torr (Δ).

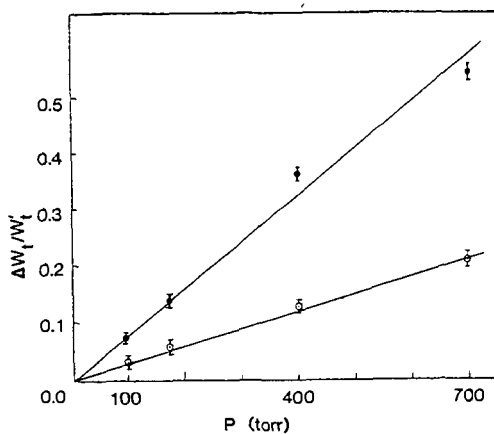


Fig 3. Ratio of amount of secondary reaction to the amount of recovered tars versus pressure. Open figures represent unwashed newsprint and solids represent 1% HCl washed newsprint.